APPLICATION FOR **UNITED STATES LETTERS PATENT**

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For:

PROCESS FOR PRODUCING A COLD-ROLLED STRIP OR SHEET OF STEEL AND STRIP OR SHEET WHICH CAN BE PRODUCED BY THE

PROCESS

PROCESS FOR PRODUCING A COLD-ROLLED STRIP OR SHEET OF STEEL AND STRIP OR SHEET WHICH CAN BE PRODUCED BY THE PROCESS

5 The invention relates to a process for producing a cold-rolled strip or sheet of steel with good deforming properties, which is subjected to recrystallizing annealing and, if appropriate, a dressing operation after hot rolling, coiling and cold rolling and has a bake-hardening potential after a subsequent deformation and for a subsequent temperature treatment.

The invention also relates to a cold-rolled strip or sheet with good deforming properties which can be produced by the process, with a bake-hardening potential after a subsequent deformation and for a subsequent temperature treatment (BH2 potential).

In automobile construction, for example, there is a need for easily deformable sheets, which must be formed relatively thin in order not to allow the weight of the vehicle to become too great. Sheets of steel of this type are generally produced in the form of a strip, in that a steel slab is cast, hot-rolled and coiled at a certain intermediate temperature. After cooling of the 25 coiled strip to essentially ambient temperature, the strip is cold-rolled to the final thickness. eliminate the stresses occurring thereby within the material, a recrystallizing annealing is carried out. Subsequently, the strip is generally gently rolled 30 of deformation between again a degree with approximately 0.5 and 2% (dressing).

The easy deformability of the steels is fundamentally at odds with an increase in the strength values of the steel grade, since the increased strength is accompanied in principle by an impairment of the easy deformability. Higher-strength steel grades (for example ZSTE and ZSTEi), which in spite of higher

strength values can be deformed relatively well, have been developed. Steel grades of this type are known, for example, as ZStE from steel-iron material sheets SEW 093 and 094 and as isotropic steel ZStRi, while the conventional "soft" steel grades are known as St12 to (corresponding to DC01, DC03, DCU4. accordance with DIN EN 10130). The steel grades differ here with regard to the addition of microalloying elements and with regard to how the process conducted. A special steel of this type is, for example, the isotropic steel ZStEi, as described in DE 38 03 064 C2, EP 0 400 031 B1 or DD 285 298 B5, the disclosure of which is incorporated as part of this description.

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For many steel grades, there is the possibility of combining good deformability with an increased yield strength after production, by producing the steel with what is known as a bake-hardening potential. hardening effect has the effect that, in a temperature treatment of the steel, as performed for example during stove-enamelling of vehicle body sheets, the strengthening is brought about, that is an increase in This is an artificial aging of the the yield strength. steel, which brings about the additional increase in strength. The increase in strength is consequently achieved after the deformation of the sheet creating the desired component has been carried out, with the result that the increase in strength does not have any adverse effect on the deformation of the sheet. It has been found that prior deformation of the sheet influences the bake-hardening effect. hardening effect brought about only by the temperature treatment, without prior deformation, is indicated as the BHo value, while a measure of the bake-hardening effect after a deformation has been performed is the BH2 value, which indicates the increase in strength after a deformation of the sheet by 2% on account of a

subsequent temperature treatment - standardized at 170°C for 20 minutes.

The bake-hardening effect is based on a content of dissolved carbon in the steel which lies above the state of equilibrium. To produce this supersaturation of with dissolved C atoms, the the steel recrystallization annealing is carried out after the cold rolling with a continuous annealing furnace. The increase in temperature in the continuous annealing furnace causes carbon to go into solution. Since the sheet is only heated up briefly in the continuous annealing furnace, a temperature distinctly above A1 is used for the recrystallization. The rapid cooling of the steel strip has the effect of producing the fraction of dissolved C atoms, which is several orders of magnitude above the state of equilibrium.

If, on the other hand, the annealing of the coiled steel strip is carried out in the bell-type furnace, 20 i.e. for a comparatively long time, and the associated slow cooling is performed in air, the steel strip remains in the state of equilibrium, with the result that no aging potential (bake-hardening potential) 25 occurs if the carbon content is ≥ 0.02%. Only when there are lower carbon contents, which can be set only by complex vacuum treatment, can an aging potential be produced, since it is only with difficulty that the C atoms in solution lead to an iron carbide precipitation 30 (cementite), on account of their low density and the associated longer diffusion paths, and therefore part remains supersaturated in solution. For C contents of ≥ 0.02%, the precipitation of the carbon takes place when there is slow cooling, with the result that no 35 dissolved carbon is available for the aging potential. The temperature treatment causes the carbon atoms in the solution to diffuse into dislocation regions of the matrix. This causes the dislocations to be blocked, with the result that an increased amount of stress is

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required to produce a plastic flow in the material This effect is increased considerably by prior again. deformation of the steel strip supersaturated with The deforming operation, for example by dissolved C. 5 deep drawing, leads to a significant increase in the dislocation density. In the case of the temperature treatment, aş performed for example enamelling, the carbon atoms diffuse into the dilated regions of the dislocations. In practice, therefore, the bake-hardening effect is relevant after a prior deformation (characterized by BH2).

Depending on the degree of deformation, the forming carried out on the sheets leads to a cold hardening (work hardening). For the use of the bake-hardening steels, the overall strength, obtained from the cold hardening resulting from the forming and the bake hardening resulting from the temperature treatment, is The known bake-hardening steels, which are produced with a continuous annealing furrace, have an approximately constant yield-strength profile for the sum of the work hardening and bake hardening over the degree of prestraining as a variable. The bakehardening effect is therefore scarcely relevant in cases of relatively great strain, on account of the highly predominant cold-hardening compon int. therefore known that the use of bake-hardening steels is predominantly of interest for components of large area which undergo only sl:.ght operations, such as for example mud guards, engine bonnets, car doors and roofs.

It is also known that the bake-hardening effect increases with the content of dissolved atoms up to a saturation value. An excessive content of dissolved C atoms leads to a lack of aging resistance of the steel sheet during age hardening. For bake-hardening steels, therefore a content of dissolved carbon of between 5 and 10 ppm is regarded as optimal.

The restriction of use of the bake-hardening effect to non-vacuum steels which have undergone recrystallizing annealing in a continuous annealing furnace leads to considerable restrictions on the production of suitable steel sheets. It has therefore not been possible in the past to produce advantageous properties of steel sheets, which preferably require recrystallizing annealing in bell-type annealing furnaces, such as for example the production of steel sheets with planar isotropy or quasi isotropy, with a bake-hardening effect.

The invention is therefore based on the problem of making possible the production of strips or sheets of steel of the type mentioned at the beginning with a bake-hardening potential which does not have the conventional restrictions.

To achieve this object, a process of the type mentioned at the beginning is characterized according to the invention in that the recrystallizing annealing is carried out in a bell-type furnace while coiled and in that the strip or sheet is subjected to looling at a cooling rate of ≥ 1°C/s after the recrystallizing annealing from a temperature T of 200°C ≤ T ≤ A₁.

This process according to the invention consequently allows the production of a bake-hardening steel strip or sheet which has undergone recrystallizing annealing in a bell-type furnace, preferably while firmly coiled, to be precise even if the C content in the steel is ≥ 0.02%.

In a surprising way, it is possible by the brief annealing according to the invention after the cooling of the recrystallizing-annealed strip or sheet to ≤ 150°C, preferably to approximately room temperature, to bring C precipitated as carbides back into solution.

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Since the temperature of the brief annealing lies below the A1 temperature of the steel, the technological properties of the steel are not otherwise significantly changed, in particular its texture, by this annealing. 5 On account of the brief annealing and the subsequent cooling, which may be performed in the Customary way with air but also with water, part of the dissolved C remains in solution and leads to the aging potential for the subsequent temperature treatment, for example during stove-enamelling.

The brief annealing is preferably brought about in a continuous annealing furnace. To produce an adequate bake-hardening effect, at a low annealing memperature T a relatively long annealing period must be maintained, while higher annealing temperatures considerably reduce the annealing period required. It has therefore preferred to use a temperature T of the brief annealing It is also preferred to set the annealing of ≥ 450°C. period of the brief annealing to between 2 minutes and 5 minutes.

It will generally be advisable to dress the strip or sheet after the brief annealing, in other words to deform it gently in the customary way. It. may also be advisable if the strip or sheet has already been dressed before the brief annealing, although this does not always appear to be required.

30 For the production of galvanized sheets or strips, it is particularly expedient to use hot galvanizing of the sheet or strip at least as part of the bring annealing. However, the process according to the invention may also be used for sheets which are not to be galvanized 35 at all or galvanized electrolytically, i.e. without the effect of heat.

The strip or sheet produced by the process according to the invention differs from conventional strips or

sheets with a bake-hardening potential in that the overall hardening of the steel (work hardening + bake hardening) increases with greater prior deforming of the sheet. Furthermore, the steel accomding to the invention contains cementite precipitations in matrix and at the grain boundaries. Customary, bake-hardening steels are . continuously-annealed virtually free from cementite. If these steels are subjected to an overaging treatment, cementite does form, but with loss of the bake-hardening effect. 10 contrast, the steel according to the invention has cementite precipitations and a bake-hardening effect. This also applies if the steel has a C content of ≥ After the stove-enamelling, the sheet has a 15 yield strength significantly increased by the bakehardening effect, i.e. by at least 15 MPa, preferably by at least 30 MPa.

The steel according to the invention may have any desired analyses known for cold-rolled strips or sheets with good deforming properties. The strip or sheet according to the invention may therefore be produced from a steel of the steel grade St12 to St15, ZStE or ZStEi.

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The steel according to the invention is preferably composed as follows:

C 0.02 to 0.12%, preferably 0.03 to 0.08%

30 Si max. 0.50%, preferably max. 0.40%

Mn 0.1 to 1.2%, preferably 0.1 to 1.0%

P max. 0.1%, preferably max. 0.08%

S max. 0.025%, preferably max. 0.02%

N max. 0.009%

35 Al 0.01 to 0.08%, preferably 0.015 to 0.08%

if appropriate, additionally: Ti 0.005 to 0.06%, preferably 0.01 to 0.04% and, if appropriate, additionally: Nb 0.005 to 0.06%, preferably 0.01 to 0.04%

- for isotropic steels -:

if appropriate, additionally:

Ti max. 0.22% and, if appropriate, in addition

5 Nb max, 0.22%

- for ZStE steels -:

remainder iron and unavoidable impurities.

Unless lower limits have been specified for the components stated above, they result from unavoidable impurities with these elements.

The steel according to the invention may have a hotgalvanized surface and have been dressed after the hot 15 galvanizing.

The brief annealing according to the invention may be performed at a constant temperature over the annealing time, but also at different annealing temperatures during the annealing period.

The invention is to be explained in more detail below on the basis of some examples.

25 Corresponding tests have been carried out with steels of the grades St15, St14, two variants of the grade ZStE220i and the grade ZStE340, the chemical compositions of which are given in the enclosed Table 1.

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Consequently, steel grades which all have a C content of $\geq 0.02\%$ were used for the tests. In the case of the steel ZStE340, the C content is even 0.075%.

35 The "soft" grades St15 and St14 have no relevant amounts of microalloying elements (Ti, V, Nb, Mo). By contrast, the isotropic steel grade ZSt220 is characterized by a titanium content which can lie between 0.01 and 0.04% and in the test examples is set

to approximately 0.02%. The higher-strength grade ZSt340 has a similar titanium content and, in addition, a significant niobium content.

5 The investigation of the steel grades St.14 and St15 yielded no relevant differences for the parameters of interest here. The same applies to the tests with the two cold strips of the grade ZStE220i. Therefore, the result of only one representative of these grades is respectively indicated and discussed below.

Since the steel grades used are commonly available on the market and therefore sufficiently known to a person skilled in the art, a person skilled in the art is familiar with the process steps required for producing 15 the steel grades and their special features for achieving the desired steel grades. It is therefore possible to dispense here with a detailed description. For the isotropic steel grades, reference is made to the production processes described in DE 38 03 064 C2, EP 0 400 031 B1 and DD 285 298 B5, the parameters of which are made the subject-matter of the disclosure of this description.

- 25 All the steel grades used were, in the customary way, cast into a slab at the required temperatures and subsequently hot-rolled. After reeling at a suitable intermediate temperature, cooling in air was performed. The cold-rolling steps were subsequently carried out.
- 30 After that, the steel strip was recrystallizingannealed in the bell-type furnace, the customary annealing period lying between 20 and 70 hours.

For some of the tests carried out here, the steel strip

35 cooled to approximately room temperature was used dressed and for some it was used undressed, before performing the brief annealing according to the invention, preferably in a continuous furrace. To be

able to establish the BH2 effect, which is all that is significant in practice, the material was prestrained.

In all cases, the cooled material was dressed after the brief annealing.

Figure 1 shows the measurement results for the BH₂ effect for the steel St15 in dependence on the annealing temperature and the annealing pariod, which was respectively set at 0.5 minutes, 2 minutes and 5 minutes. The specimens not dressed before the annealing have been designated "1 x dressed", because of the dressing after the annealing, the predressed specimens as "2 x dressed".

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It is evident that, already at the annealing temperature of 200°C and with a short annealing period, there is an increased BH₂ potential, which rises for all the specimens with increasing annealing temperature and increasing annealing period, with no increase, or no significant increase, in the BH₂ potential being achieved any longer at the annealing temperature of 700°C by prolonging the annealing period beyond 2 minutes.

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For all the specimens, the dressing of the material before the brief annealing does not produce any notable increase in the BH₂ effect, in some cases there is even a notable decrease.

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Figure 2 shows the results for the same investigations in the case of the steel ZStE220i. A very great BH2 effect is obtained with an annealing temperature of 700°C and an annealing period of 2 minutes. Prolonging the annealing period at this temperature leads to a reduction in the BH2 effect. Here, too, dressing before the brief annealing tends to be harmful for the magnitude of the BH2 effect.

The results represented in Figure 3 for the steel grade ZStE340 clearly illustrate that for this case the dressing before the brief annealing is favourable, at least for average annealing temperatures. With the low annealing temperature of 200°C, a maximum is obtained with the annealing period of 2 minutes for the 1 \times dressed steel. For shorter and longer annealing periods, the BH₂ effect even goes back to 0.

Figures 4 to 6 clearly illustrate the dependence of the BH value on the degree of prior straining of the material. In all cases, a more or less clearly defined maximum is formed with approximately 2% degree of straining, while conventional bake—hardening steels have a BH value which falls as the degree of straining increases.

Figure 4 shows the results for undressed specimens of the grades ZSt220i, St14 and ZSt340, which have been annealed for 5 minutes at 500°C and deformed between 0.5 and 1% during dressing, dependent on the steel grade. The bake-hardening annealing took place in accordance with the testing specifications at 170°C for 20 minutes.

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The results represented in Figure 5 relate to the same steels with the same degrees of dressing, but the brief annealing having been performed at 500°C for an annealing period of 15 minutes.

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The results represented in Figure 6 relate to the steel grades treated in the same way, which were annealed at 700°C for 5 minutes. What is striking here is the high bake-hardening potential for the isotropic steel grade ZStE220i, which was prestrained with a degree of deformation of between 2 and 3%.

In Figure 7, for the three steel grades, the sum of the work hardening (WH) and the bake hardening (BH) is

indicated in dependence on the degree of straining. While conventional bake-hardening steel grades show an essentially constant sum of the rise in yield strength over the different degrees of straining, the steel grades according to the invention have a rise in yield strength which increases with the degree of straining. The steels treated according to the invention therefore differ perceptibly in their mechanical properties from the conventionally produced bake-hardening steels.

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Figures 8 to 10 clearly illustrate the profile of the work-hardening curve and of the bake-hardening curve in dependence on the degree of prestraining for the steel grades St15 (Figure 8), ZStE220i (Figure 9) and ZStE340 (Figure 10). While the pure bake-hardening effect tends to decrease again with increasing prestraining, the work-hardening effect increases disproportionately, resulting in the rising cumulative curve for the steel according to the invention.

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Figure 11 clearly illustrates the dependence of the sum of the rise in yield strength on the annealing For all the temperatures and the annealing periods. steel grades, the highest rise in yield strength is obtained with the highest (permissible) 700°C with approximately temperature of annealing period (5 minutes). A further increase in the annealing temperature is not possible, since the ${\tt A}_{\tt l}$ value (approximately 720°C) must not be exceeded during Exceeding the A₁ temperature the annealing operation. would cause transformations which would adversely change the properties of the steel.

The main mechanical values for steels treated according to the invention with a BH₂ effect are compared in Table 2 with the mechanical properties of the steel grades as they are presented in the European standard EN 10 130, in a material sheet W5/94 of the Applicant

or in the steel-iron material sheets SEW 093 and SEW 094.

All percentages given are % by weight: